(1) JP. 2872899, B

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 07-149536
(43)Date of publication of application : 13.06.1995

(51)Int.Cl. C03C 3/064
C03C 3/089
G02B 3/00

(21)Application number : 05-321155
(22)Date of filing : 26.11.1993

(71)Applicant : OHARA INC
(72)Inventor : ONOZAWA MASAHIRO

(54) OPTICAL GLASS

(57)Abstract:
PURPOSE: To obtain an optical glass having a good chemical resistance while maintaining prescribed optical constants and a yield point suitable for a mold press process, by using SiO2, B2O3, SrO and Li2O as essential components and specifying the other components to limit compositions of the components.
CONSTITUTION: An optical glass contains components in ranges of composition in wt.% as SiO2: 25-50%, B2O3: 16-40%, Al2O3: 0-5%, TiO2: 0-1%, ZrO2: 0-5%, ZnO: 0-5%, MgO: 0-5%, CaO: 0-8%, SrO: 5-25%, BaO: 0-9%, Li2O: 1-10%, Na2O+ K2O: 0-5% and Sb2O3: 0-1%, and also has optical constants within certain ranges such as a refractive index (Nd) of 1.55-1.65, and an Abbe number (ν d) of 55-63. Also to improve melting property and devitrification resistance of the glass, the other components than shown above, e.g. La2O3, Bi2O3, Cs2O, SnO, F, etc., may be added, as necessary.

LEGAL STATUS

[Date of request for examination]	25.01.1996
[Date of sending the examiner's decision of rejection]	
[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]	
[Date of final disposal for application]	
[Patent number]	2872899
[Date of registration]	08.01.1999
[Number of appeal against examiner's decision of rejection]	
[Date of requesting appeal against examiner's decision of rejection]	
[Date of extinction of right]	

CLAIMS

---

(57) [Claim(s)]
[Claim 1] At weight %, it is SiO2. 25 - 50%, B-2 O3 16 - 40%, aluminum 2O3 0 - 5%, TiO2 0 - 1%, ZrO2 0 - 5%, Less than 0 - 5% of ZnO(s), MgO 0 - 5%, CaO 0 - 8%, SrO 11 - 25%, BaO 0 - 6%, Li2O 1 - 10%, Na2O+K2O 0 - 5%, and Sb 2O3 It consists of each component of 0 - 1% of range. Optical glass characterized by for a refractive index (Nd) having 1.55 to less than 1.63, and the Abbe number (nud) having the optical constant of the range of 59-63.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] this invention relates to less than [refractive-index (Nd)1.55-1.63] and the optical constant of the range of the Abbe numbers (nud) 59-63, and the optical glass of the SiO2-B-2O3-SrO-Li2O system which has the outstanding chemical durability to an acid, i.e., acid resistance, and a low-temperature softening degree.
[0002]
[Description of the Prior Art] From the former, the heavy crown system glass which has the aforementioned optical constant is known variously, for example, much SK (shot catalog name) type glass is indicated in "a glass composition data book and 1991 (Glass Manufactures' Association of Japan issue)." However, these glass is unsuitable as glass for a mould press for fabricating directly the optical element to which molding temperature does not need grinding or polish after press forming by becoming high, in order that a surrendering point (At) may generally exceed 600 degrees C highly. Since problems, such as the endurance of mold material, will arise if molding temperature becomes an elevated temperature in a mould press, the surrendering point of glass has an as much as possible desirable method of a low. In order to solve these problems, the glass of the system which introduced R'2O (R' is alkali metal) is proposed [******]. For example, although what made TeO2 component indispensable is indicated by JP,4-292435,A since chemical durability becomes bad when R'2O is only introduced into composition of the conventional SiO2-B-2O3-BaO system, this glass has bad acid resistance. Moreover, since acid resistance tends to produce YAKE on a glass front face bad like the above, the thing of the SiO2-B-2O3-CaO-Li2O system currently indicated by JP,60-122747,A is unsuitable as glass for a mould press.
[0003]
[Problem(s) to be Solved by the Invention] this invention aims at offering the optical glass which has the outstanding chemical durability to an acid, maintaining the surrendering point (At) of having been suitable for less than [refractive-index (Nd)1.55-1.63], and the optical constant and mould press of the range of the Abbe numbers (nud) 59-63.
[0004]
[Means for Solving the Problem] the optical glass which this invention person has the aforementioned predetermined optical constant in the SiO 2-B-2 O 3-SrO-Li 2 O system glass of the specific range which is not specifically indicated by the Prior art as a result of it repeated test research wholeheartedly in order it attains the above-mentioned purpose, and has the low-temperature softening degree suitable for a mould press, i.e., the outstanding chemical durability to the point surrendering [low] and an acid, is obtained -- **** -- it came make a broth and this invention
[0005] The feature of the optical glass concerning this invention is weight %, and is SiO2. 25 - 50%, B-2 O3 16 - 40%, aluminum 2O3 0 - 5%, TiO2 0 - 1%, 20 - 5% of ZrO(s), ZnO Less than 0 - 5%, MgO 0 - 5%, CaO 0 - 8%, SrO 11 - 25%, BaO 0 - 6%, Li2O 1 - 10%, Na2O+K2O 0 - 5%, and Sb 2O3 It is in the place which consists of each component of 0 - 1% of range, and has less than [refractive-index (Nd)1.55-1.63] and the optical constant of the range of the Abbe numbers (nud) 59-63.
[0006] The reason which limited the composition range of each component is as above-mentioned as follows. When the chemical durability of glass falls that the amount is less than 25% and the amount exceeds 50%, while it becomes impossible for a low-temperature softening degree to maintain SiO2 component, it becomes impossible that is, to maintain the optical constant made into the target of this invention. Although B-2O3 component is a component effective in giving a low-temperature softening degree to glass, if devitrification-proof nature gets worse at less than 16% and the amount exceeds 40%, chemical durability will get worse. 2Oaluminum3 component is effective in improvement in the chemical durability of glass. However, elevation of submission temperature (At) is imitated at the same time devitrification-proof nature will get worse, if the amount exceeds 5%, and it is **.
[0007] Although TiO2 component can be added because of solar RIZESHON prevention of glass and optical constant adjustment, 1% or less is enough as the amount. Although ZrO2 component can be added if needed since it raises a refractive index and improves chemical durability, if it exceeds 5%, devitrification-proof nature will get worse. [0008] a SrO component shows the outstanding acid resistance, maintaining a low-temperature softening degree by coexisting with B-2O3 component of the specific range in this invention -- **** -- it is the important component which took out it is the conventional glass composition system which has the aforementioned optical constant, and although the SrO component was used for adjustment of an optical constant etc. as a component which shows the same property as BaO and CaO, SrO components are low dispersibility and chemical durability, and a still more advantageous synthetic component in respect of a low-temperature softening degree compared with other divalent metal oxide components in raising the refractive index of glass by this composition system -- **** -- it took out A lot of introduction was conventionally difficult for the SrO component in order to worsen the stability of glass. However, very stable glass was able to be obtained by making the B-2O3 aforementioned component 16% or more. In order to obtain the chemical durability and the low-temperature softening degree which were excellent as above-mentioned, maintaining the stability of glass, acid resistance becomes 11 - 25% of the amount is effective, and inadequate at less than 11%, and if it exceeds 25%, glass will become unstable on the contrary. Although it can add because of optical constant adjustment etc., while the stability of glass becomes is it easy to be spoiled that the amount of a ZnO component is 5% or more as for ZnO, MgO, CaO, and the BaO component which are other divalent metal oxide components, chemical durability gets worse. Moreover, if the amount of MgO, CaO, and a BaO component exceeds 5%, 8%, and 6%, respectively, while the stability of glass will become is easy to be spoiled, chemical durability gets worse.
[0009] since especially the effect of giving a low-temperature softening property to glass is large, a Li2O component is an

important component -- in order to demonstrate the effect, maintaining the devitrification-proof nature of glass, you should make the amount 1 - 10% of range Although a Na2O and K2O component may be made to add if needed in order to acquire a low-temperature softening property, the amount should carry out those total quantities to 5% or less for devitrification-proof nature and chemical durability maintenance. Although 2OSb3 component can be arbitrarily added as a clarifier in the case of glass melting, less than 1% is enough as the amount.

[0010] [Example] Next, it was shown in Table 1 with the refractive index (Nd) of the glass obtained, respectively about the example of operation composition concerning the optical glass of this invention (No.1-No.5), and the example of comparison composition of the aforementioned conventional optical glass (No.A-No.C), the Abbe number (nud), the surrendering point (At, **), and the measurement test result of chemical durability.

[0011] The acid-proof sex test is immersed for 30 minutes into 3N-nitric-acid solution (25 degrees C) in each glass sample (about 30x30x5mm) which has the fracture surface and a polished surface. that by which the erosion degree of both front faces is observed, it is changeless also on the surface of any, and transparency was maintained -- O mark -- displaying -- moreover, both front faces -- all adopted the method of displaying that by which the dry area was produced and transparency was spoiled by whether it is Ming by x mark In addition, after these glass samples carry out weighing capacity mixture of the usual raw materials for optics, such as an oxide, a carbonate, a nitrate, and a hydroxide, at a predetermined rate, they are supplied to a platinum crucible, and after fusing for about 2 to 4 hours and carrying out stirring homogenization at the temperature of 1150-1350 degrees C according to the difficulty of melting by composition, they can be easily obtained by casting and cooling slowly to metal mold etc.

[0012]

[Table 1]

単位；重量%

	実施例					比較例		
No.	1	2	3	4	5	A	B	C
SiO_2	27.4	42.0	44.0	46.8	50.0	38.7	42.0	45.8
B_2O_3	40.0	24.0	23.0	19.6	16.0	14.9	24.0	12.0
Al_2O_3		1.0	3.0			5.0	1.0	4.0
TiO_2	1.0		0.2		0.1			
ZrO_2			1.0					
ZnO	4.6	3.0	1.6		1.8			8.0
CaO	7.0		3.0		3.0			20.0
SrO	11.0	22.8	17.1	24.5	20.6			
BaO	2.0					40.1	22.8	
Li_2O	6.0	7.0	7.0	9.0	8.0		7.0	5.0
Na_2O								5.0
Sb_2O_3	1.0	0.2	0.1	0.1	0.5	1.0	0.2	0.2
As_2O_3						0.3		
TeO_2							3.0	
n d	1.5944	1.5834	1.5792	1.5868	1.5886	1.5891	1.5818	1.5910
ν d	59.7	62.7	61.8	62.9	61.7	61.3	62.8	57.0
A t	537	541	549	532	533	650	540	549
耐酸性	○	○	○	○	○	○	×	×

[0013] Each glass of the example of this invention has a predetermined optical constant and the predetermined point (At) surrendering [low], and, moreover, improves much more rather than the conventionally well-known, acid resistance, i.e., the chemical durability to an acid, example glass of comparison as it sees in Table 1. Moreover, each of these glass is excellent in devitrification-proof nature, and it is easy to homogenize it. For this reason, the glass of the above-mentioned example is easy to manufacture, and suitable as a material for a mould press.

[0014]

[Effect of the Invention] Since the optical glass of this invention has specific composition of a SiO2-B-2O3-SrO-Li2O system, it has less than [refractive-index (Nd)1.55-1.63], and the optical constant and the point (At) surrendering [low] of the range of the Abbe numbers (nud) 59-63, and the chemical durability to an acid is excellent much more compared with conventional glass, as stated above. Moreover, manufacture is easy, and it is easy to homogenize, and is suitable for the mould press.

[Translation done.]

(1) JP, 2872899, B

(19)日本国特許庁（ＪＰ）　(12)特　許　公　報（Ｂ２）　(11)特許番号

第2872899号

(45)発行日　平成11年(1999)３月24日　(24)登録日　平成11年(1999)１月８日

(51)Int.Cl.[6]	識別記号	ＦＩ
Ｃ０３Ｃ	3/064	Ｃ０３Ｃ　3/064
	3/089	3/089
Ｇ０２Ｂ	3/00	Ｇ０２Ｂ　3/00

請求項の数１(全 3 頁)

(21)出願番号　特願平5－321155

(22)出願日　平成５年(1993)11月26日

(65)公開番号　特開平7－149536

(43)公開日　平成７年(1995)６月13日

審査請求日　平成８年(1996)１月25日

(73)特許権者　000128784
株式会社オハラ
神奈川県相模原市小山１丁目15番30号

(72)発明者　小野沢　雅浩
神奈川県相模原市小山１丁目15番30号
株式会社オハラ内

(74)代理人　弁理士　坂本　徹　(外１名)

審査官　前田　仁志

(56)参考文献　特開　昭54－3115（ＪＰ，Ａ）
特開　平４－292435（ＪＰ，Ａ）
特開　昭60－122747（ＪＰ，Ａ）

(58)調査した分野(Int.Cl.[6]，ＤＢ名)
C03C　3/064
C03C　3/089
G02B　3/00

(54)【発明の名称】　光学ガラス

(57)【特許請求の範囲】

【請求項１】　重量%で、SiO_2　２５～５０%、B_2O_3　１６～４０%、Al_2O_3　０～５%、TiO_2　０～１%、ZrO_2　０～５%、ＺｎＯ０～５%未満、ＭｇＯ　０～５%、ＣａＯ　０～８%、ＳｒＯ　１１～２５%、ＢａＯ　０～６%、Li_2O　１～１０%、Na_2O+K_2O　０～５%およびSb_2O_3　０～１%の範囲の各成分からなり、屈折率（Ｎｄ）が１．５５～１．６３未満、アッベ数（νｄ）が５９～６３の範囲の光学恒数を有することを特徴とする光学ガラス。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】本発明は、屈折率（Ｎｄ）１．５５～１．６３未満及びアッベ数（νｄ）５９～６３の範囲の光学恒数と、酸に対する優れた化学的耐久性、すなわち、耐酸性及び低温軟化性を有する$SiO_2-B_2O_3-SrO-Li_2O$系の光学ガラスに関する。

【０００２】

【従来の技術】従来から、前記の光学恒数を有する重クラウン系ガラスが種々知られており、例えば「ガラス組成データブック・１９９１年（（社）日本硝子製品工業会発行）」には、ＳＫ（ショットカタログ名称）タイプのガラスが多数記載されている。しかし、これらのガラスは、一般に屈伏点（Ａｔ）が高く６００℃を超えるため成形温度が高くなり、プレス成形後に研削または研磨を必要としない光学素子を直接成形するためのモールドプレス用ガラスとしては不適当である。モールドプレスにおいて成形温度が高温になると型材の耐久性等の問題が生じるため、ガラスの屈伏点は可能なかぎり低い方が望ましい。これらの問題を解決するためとして、R'_2

Ｏ（Ｒ'はアルカリ金属）を導入した系のガラスが提案されている。例えば特開平４－２９２４３５号公報には、従来のＳｉＯ₂－Ｂ₂Ｏ₃－ＢａＯ系の組成にＲ'₂Ｏを単に導入した場合、化学的耐久性が悪くなるため、ＴｅＯ₂成分を必須としたものが開示されているが、このガラスは耐酸性が悪い。また特開昭６０－１２２７４７号に開示されているＳｉＯ₂－Ｂ₂Ｏ₃－ＣａＯ－Ｌｉ₂Ｏ系のものは、上記と同様に耐酸性が悪くガラス表面にヤケを生じやすいため、モールドプレス用のガラスとしては不適当である。

【０００３】

【発明が解決しようとする課題】本発明は、屈折率（Ｎｄ）１．５５～１．６３未満及びアッベ数（νｄ）５９～６３の範囲の光学恒数とモールドプレスに適した屈伏点（Ａｔ）を維持しつつ、酸に対する優れた化学的耐久性を有する光学ガラスを提供することを目的とする。

【０００４】

【課題を解決するための手段】上記目的を達成するため本発明者は、鋭意試験研究を重ねた結果、従来の技術には具体的には開示されていない特定範囲のＳｉＯ₂－Ｂ₂Ｏ₃－ＳｒＯ－Ｌｉ₂Ｏ系ガラスにおいて、前記所定の光学恒数を有し、モールドプレスに適した低温軟化性、すなわち低い屈伏点と酸に対する優れた化学的耐久性を有する光学ガラスが得られることをみいだし、本発明をなすに至った。

【０００５】本発明にかかる光学ガラスの特徴は、重量％で、ＳｉＯ₂　２５～５０％、Ｂ₂Ｏ₃　１６～４０％、Ａｌ₂Ｏ₃　０～５％、ＴｉＯ₂　０～１％、ＺｒＯ₂　０～５％、ＺｎＯ　０～５％未満、ＭｇＯ　０～５％、ＣａＯ　０～８％、ＳｒＯ　１１～２５％、ＢａＯ　０～６％、Ｌｉ₂Ｏ　１～１０％、Ｎａ₂Ｏ＋Ｋ₂Ｏ　０～５％およびＳｂ₂Ｏ₃　０～１％の範囲の各成分からなり、かつ、屈折率（Ｎｄ）１．５５～１．６３未満、アッベ数（νｄ）５９～６３の範囲の光学恒数を有するところにある。

【０００６】上記のとおり、各成分の組成範囲を限定した理由は次のとおりである。すなわちＳｉＯ₂成分は、その量が２５％未満であるとガラスの化学的耐久性が低下し、またその量が５０％を超えると低温軟化性が維持し得なくなるとともに、本発明の目標とする光学恒数を維持できなくなる。Ｂ₂Ｏ₃成分はガラスに低温軟化性を与えるのに有効な成分であるが、その量が１６％未満では耐失透性が悪化し、４０％を超えると化学的耐久性が悪化する。Ａｌ₂Ｏ₃成分は、ガラスの化学的耐久性の向上に有効である。しかし、その量が５％を超えると耐失透性が悪化すると同時に屈伏温度（Ａｔ）の上昇をまねく。

【０００７】ＴｉＯ₂成分は、ガラスのソーラリゼーション防止と光学恒数調整のため添加し得るが、その量は１％以下で十分である。ＺｒＯ₂成分は、屈折率を高め

化学的耐久性を改善するため必要に応じ添加し得るが、５％を超えると耐失透性が悪化する。

【０００８】ＳｒＯ成分は、本発明において特定範囲のＢ₂Ｏ₃成分と共存することにより、低温軟化性を維持しつつ、優れた耐酸性を示すことをみいだした重要な成分である。前記の光学恒数を有する従来のガラス組成系で、ＳｒＯ成分はＢａＯ、ＣａＯと同じ性質を示す成分として光学恒数の調整等に用いられていたが、本組成系でＳｒＯ成分はガラスの屈折率を高めるうえ、他の２価金属酸化物成分と比べ、低分散性及び化学的耐久性、さらに低温軟化性の点で総合的に最も有利な成分であることをみいだしたのである。従来ＳｒＯ成分はガラスの安定性を悪化させるため、多量の導入が困難であった。ところが前記のＢ₂Ｏ₃成分を１６％以上にすることで極めて安定なガラスを得ることができたのである。上記のとおり、ガラスの安定性を維持しつつ優れた化学的耐久性及び低温軟化性を得るためには、その量は１１～２５％が有効であり、１１％未満では耐酸性が不十分となり、２５％を超えるとかえってガラスが不安定になる。他の２価金属酸化物成分であるＺｎＯ、ＭｇＯ、ＣａＯ及びＢａＯ成分は、光学恒数調整等のため添加し得るが、ＺｎＯ成分の量が５％以上であるとガラスの安定性が損なわれやすくなると同時に化学的耐久性が悪化する。また、ＭｇＯ、ＣａＯ及びＢａＯ成分の量が、それぞれ５％、８％及び６％を超えるとガラスの安定性が損なわれやすくなると同時に化学的耐久性が悪化する。

【０００９】Ｌｉ₂Ｏ成分は、ガラスに低温軟化特性を与える効果が特に大きいので重要な成分であるが、ガラスの耐失透性を維持しつつその効果を発揮させるためには、その量は１～１０％の範囲にすべきである。Ｎａ₂Ｏ及びＫ₂Ｏ成分は、低温軟化特性を得るために必要に応じ添加させ得るが、その量は耐失透性と化学的耐久性維持のため、それらの合計量を５％以下にすべきである。Ｓｂ₂Ｏ₃成分は、ガラス溶融の際の清澄剤として任意に添加し得るが、その量は１％以内で十分である。

【００１０】

【実施例】次に、本発明の光学ガラスにかかる実施組成例（Ｎｏ．１～Ｎｏ．５）及び前記従来の光学ガラスの比較組成例（Ｎｏ．Ａ～Ｎｏ．Ｃ）についてそれぞれ得られたガラスの屈折率（Ｎｄ）、アッベ数（νｄ）、屈伏点（Ａｔ、℃）及び化学的耐久性の測定試験結果とともに表１に示した。

【００１１】耐酸性試験は、破面及び研磨面を有する各ガラス試料（約３０×３０×５ｍｍ）を３Ｎ－硝酸水溶液（２５℃）中に３０分間浸漬して両表面の浸蝕度合を観察し、いずれの表面にも変化がなく透明性が維持されたものを○印で表示し、また両表面いずれも荒れを生じ透明性が明かに損なわれたものを×印で表示する方法を採用した。なお、これらのガラス試料は酸化物、炭酸塩、硝酸塩、水酸化物等の通常の光学用原料を所定の割

合で秤量混合した後白金坩堝に投入し、組成による溶融の難易度に応じて１１５０～１３５０℃の温度で約２～４時間溶融し、撹拌均質化した後、金型等に鋳込み徐冷＊

＊することにより容易に得ることができる。

【００１２】

【表１】

単位；重量%

	実施例					比較例		
Ｎｏ.	1	2	3	4	5	A	B	C
SiO_2	27.4	42.0	44.0	46.8	50.0	38.7	42.0	45.8
B_2O_3	40.0	24.0	23.0	19.6	16.0	14.9	24.0	12.0
Al_2O_3		1.0	3.0			5.0	1.0	4.0
TiO_2	1.0		0.2		0.1			
ZrO_2			1.0					
ZnO	4.6	3.0	1.6		1.8			8.0
CaO	7.0		3.0		3.0			20.0
SrO	11.0	22.8	17.1	24.5	20.6			
BaO	2.0					40.1	22.8	
Li_2O	6.0	7.0	7.0	9.0	8.0		7.0	5.0
Na_2O								5.0
Sb_2O_3	1.0	0.2	0.1	0.1	0.5	1.0	0.2	0.2
As_2O_3						0.3		
TeO_2							3.0	
ｎｄ	1.5944	1.5834	1.5792	1.5868	1.5886	1.5891	1.5818	1.5910
νｄ	59.7	62.7	61.8	62.9	61.7	61.3	62.8	57.0
Ａｔ	537	541	549	532	533	650	540	549
耐酸性	○	○	○	○	○	○	×	×

【００１３】表１にみられるとおり、本発明の実施例のガラスはいずれも所定の光学恒数と低い屈伏点（Ａｔ）とを有し、しかも耐酸性、すなわち、酸に対する化学的耐久性が従来公知の比較例ガラスよりも一段と改善されている。また、これらのガラスはいずれも耐失透性に優れ、また均質化しやすい。このため上記実施例のガラスは製造が容易であり、モールドプレス用素材として適している。

【００１４】

【発明の効果】以上に述べたとおり、本発明の光学ガラスは$SiO_2-B_2O_3-SrO-Li_2O$系の特定組成を有するものであるから、屈折率（Ｎｄ）１．５５～１．６３未満、アッベ数（νｄ）５９～６３の範囲の光学恒数と低い屈伏点（Ａｔ）とを有し、かつ、従来のガラスに比べて酸に対する化学的耐久性が一段と優れている。また、製造が容易であり、均質化しやすく、モールドプレスに適している。